

Characterization and stability of doped SnO₂ anodes

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Doped tin dioxide electrodes have been prepared by a standard spray pyrolysis technique. The electrochemical behaviour of these electrodes has been investigated by cyclic voltammetry in sulphuric acid using the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple system as test reaction. Oxygen evolution has been used to study the stability of doped SnO₂ electrodes. The SnO₂ electrodes doped with antimony and platinum exhibit the highest stability. XPS analysis shows that the oxidation state of Sn, Sb and Pt are +4, +3 and +2, respectively, the probable species being SnO₂, Sb₂O₃ and PtO.

Keywords: *SnO₂ anodes, doping, high overvoltage anodes, surface analysis, oxidation, water treatment*

1. Introduction

There are several methods for treating industrial wastewater containing organic and inorganic pollutants: biological treatment, incineration, adsorption, chemical and electrochemical oxidation and/or reduction.

Although biological processes are the easiest and the most economic processes for wastewater treatment, their application is not always possible, especially for effluents with high concentrations of organic or toxic compounds. In such cases, the introduction of previous chemical or electrochemical oxidation stages has become an attractive alternative for the treatment of wastewater effluents. Electrochemical oxidation methods have proved to be more efficient than chemical ones for removal of some organic pollutants (i.e., phenolic compounds). Thus, chemical oxidation of phenol by ozone or hydrogen peroxide with Fe^{2+} as catalyst yields 30% reduction in TOC (total organic carbon) [1, 2]. In contrast, the use of electrochemical oxidation methods results in a 38% and 90% TOC removal when platinum and doped SnO₂ are employed, respectively [3–8]. Kötzt *et al.* [5, 6] were the pioneers in the study of physical and electrochemical properties of doped SnO₂ anodes. These electrodes present a low resistivity, high chlorine and oxygen evolution overpotentials, a high exchange current density for the $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$ reaction and an efficiency and a rate of phenol removal much higher than for Pt and PbO₂.

The higher TOC removal when electrochemical oxidation methods are used have been attributed by Comninellis and Pulgarin [7, 8] to the oxidation of phenol and intermediate products to CO₂.

Thus, an adequate electrode for the elimination of organic pollutants should present a high oxygen overpotential, a high electrical conductivity and also good stability. The doped SnO₂ electrode satisfies these requirements.

The aims of this work are twofold: the preparation of stable electrodes for oxidative purposes and the characterization of SnO₂ electrodes doped with antimony or antimony and platinum. The techniques used to characterize the electrodes were scanning electron microscopy (SEM), energy dispersion X-ray (EDX), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry.

2. Experimental details

2.1. Electrode preparation

Several metal substrates, temperatures and solvents were tested for the preparation of the doped SnO₂ electrodes [9, 10]. Due to the fact that the best results obtained by us have been using Ti and ethanolic solutions, the present study will focus on this material and solution.

Doped Ti/SnO₂ electrodes were prepared by a standard spray-pyrolysis method [5, 11, 12]. The spray solution used for the preparation of the SnO₂ electrode doped with antimony was 10 g SnCl₄·5H₂O and 1 g SbCl₃ in 100 ml of ethanol–HCl mixture; the same solution with 1 g Pt (2.1% H₂PtCl₆) was used for obtaining the best platinum and antimony doped electrodes. The titanium substrate, a wire of 0.5 mm diameter (99.6% of purity, Goodfellow Metals), was previously etched in a 10% oxalic acid solution for 1 h, then rinsed with water and heated to 400 °C. The ethanolic solution was then sprayed onto the titanium with an air-atomizing spray at a fixed distance of

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40 cm. Then, the electrode was heated for 10 min at 400 °C. The above operation was repeated at least five times. The thickness of the doped SnO₂ films depends on the number of spray-pyrolysis sequences. Finally, further heat treatment for 1 h at 600 °C was carried out.

The same experimental procedure was used for the preparation of electrodes with sheet and expanded titanium substrates (IMI 125 type, INAGASA).

2.2. Electrode characterization

Different techniques were applied to characterize the properties of the doped SnO₂ electrodes. The electrochemical behaviour of doped SnO₂ electrodes was studied by cyclic voltammetry. The voltammograms were obtained with a standard set-up using a potentiostat (HQ Instruments, model 101), a generator (EG&G PARC, model 175) and an X-Y recorder (Philips PM 8133). The electrolyte was a 0.5 M sulphuric acid solution prepared from Merck suprapur and Millipore water or a 0.5 M H₂SO₄ + 5 × 10⁻² M FeSO₄ (Merck p.a.) solution. The solutions were deoxygenated by bubbling nitrogen (N-50) before each experiment and an inert atmosphere was maintained over the working solution during the experiment. The counter electrode was a platinum wire and the potentials were measured versus a reversible hydrogen electrode immersed in 0.5 M sulphuric acid and connected to the cell through a Luggin capillary. The cyclic voltammograms were usually recorded at room temperature at a sweep rate of 50 mV s⁻¹.

Surface analysis was performed by X-ray photoelectron spectroscopy (XPS) using a ESCALAB 210 spectrometer. The X-ray source was MgK_α of energy 1253.6 eV with a power of 240 W. The samples were placed on 'posiloc' standard sample holders. A binding energy (BE) of 284.9 eV, corresponding to the C 1s peak was used as an internal standard. The pressure in the analysis chamber was maintained below 2 × 10⁻⁹ mbar during the measurements.

Scanning electron microscopy (SEM) was employed to observe the surface morphology of the electrodes using a Jeol (JSM 840). SEM also provided information on the different elements present on the surface using the energy dispersive X-ray detector (Link QX 200 EDX).

The thickness of the coatings were determined by the step method using a profilometer (Surfometer SF 220).

2.3. Stability test

The oxygen evolution reaction was used to study the stability of doped SnO₂ electrodes in 0.5 M H₂SO₄ or 0.5 M K₂SO₄ (Merck p.a.) solutions. The potential versus time curves of the doped SnO₂ electrodes at constant current density (referred to a geometric area of the electrode of 0.08 cm²) depends on the polarization time and on the previous history of the electrode. An increase of 1 V in the potential was adopted

as an indication of the loss of electrocatalytic activity of doped SnO₂ electrodes [13]. This potential increase can be produced by the formation of a passivated surface layer, probably caused by the hydration of the SnO₂ layer and/or the passivation of the layer-substrate interface [5, 14].

3. Results and discussion

3.1. SnO₂ electrodes doped with antimony

Figure 1 (solid line) shows the voltammogram recorded in a 0.5 M H₂SO₄ solution for a SnO₂ electrode doped with antimony with a five spray-pyrolysis sequence. The voltammogram is featureless in this potential range and little information is obtained about the composition and behaviour of the electrode surface. At potentials below 0.3 V the onset of a cathodic process becomes evident. The current associated with this process increases with decreasing potential and eventually overlaps the hydrogen evolution current. No peaks or waves appear before oxygen evolution, which begins at approximately 2.2 V. Compared to the behaviour observed for a platinum electrode in the same electrolyte and for the same current density, oxygen evolution is shifted positively about 500 mV.

To check the charge transfer rate through the doped SnO₂ electrode-electrolyte interface, the voltammetric behaviour of the redox system Fe³⁺/Fe²⁺ was studied. From the value of the peak potential and from the value of the difference between the potential of the anodic and cathodic peaks (ΔE_p), a direct estimate of the reversibility of the system, that is, the electron transfer rate, could be obtained. Figure 2 shows the stabilized voltammogram obtained with this electrode for a 0.5 M H₂SO₄ + 5 × 10⁻² M FeSO₄ solution at 50 mV s⁻¹. Well defined reduction and oxidation peaks are observed at about 0.65 and 0.75 V, respectively. The potentials of the anodic (E_p^a) and cathodic (E_p^c) peaks shift with scan rate, increasing the value of E_p^a - E_p^c = ΔE_p. The peak separation, from 96 to 120 mV (for 50 and 200 mV s⁻¹, respectively), is always greater than that expected for a reversible one-electron process (ΔE_p = 59 mV). However, the doped SnO₂ electrode behaves better than a platinum electrode at all scan rates (ΔE_p values from 104 to 136 mV).

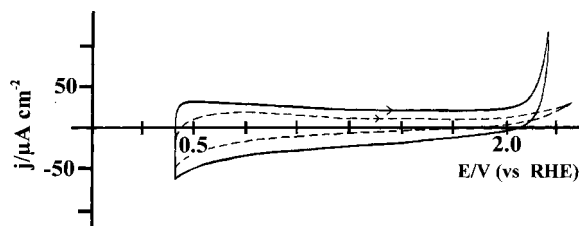


Fig. 1. Voltammograms for a SnO₂ electrode doped with antimony with five spray-pyrolysis sequence in 0.5 M H₂SO₄. $\nu = 50 \text{ mV s}^{-1}$. (—) before and (---) after 5 h of electrolysis at 10 mA cm^{-2} in 0.5 M H₂SO₄.

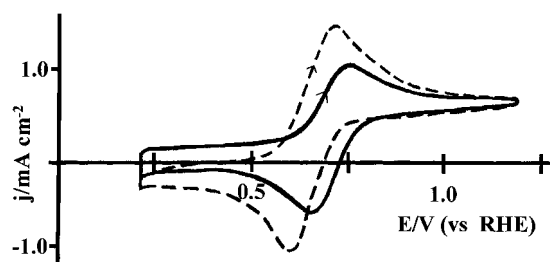


Fig. 2. Voltammetric behaviour of a SnO_2 electrode doped with antimony (—) and with antimony and platinum (0.2%) (---) with a five spray-pyrolysis sequence in $5 \times 10^{-2} \text{ M. FeSO}_4 + 0.5 \text{ M H}_2\text{SO}_4$ solution. $\nu = 50 \text{ mV s}^{-1}$.

The SEM photomicrographs of the surface of the SnO_2 electrode doped with antimony are shown in Fig. 3. These figures show a slightly rough surface, with the particles of SnO_2 small and uniformly distributed.

The presence and distribution of Sn and Sb on the electrode were studied by EDX. The results indicate a homogeneous distribution of the components (Sn, Sb) on the electrode. Sn and Sb are detected in a proportion of 23.5% and 6%, respectively, while titanium is detected at 66.6%. This detection indicates that the thickness of the SnO_2 film is, according to Rosinskaya *et al.* [15], lower than $2 \mu\text{m}$.

Profilometric measurements were carried out on a titanium sheet partially covered with SnO_2 doped with antimony (five spray-pyrolysis sequences). A coating thickness lower than $1 \mu\text{m}$ is obtained. This result is in agreement with that obtained from EDX

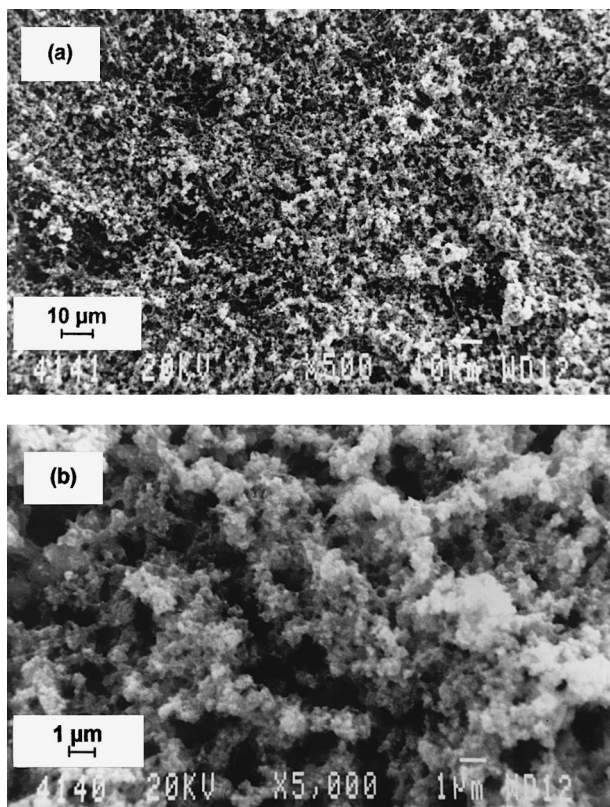


Fig. 3. Scanning electron micrograph of a SnO_2 electrode doped with antimony with a five spray-pyrolysis sequence.

measurements. Thus, it can be concluded that SnO_2 films formed by a five spray pyrolysis sequence are very thin. The holes created during the pre-treatment of titanium (holes from 3 to $6 \mu\text{m}$ have been previously observed using this pre-treatment [9]) are mainly covered during spray pyrolysis.

From the electrochemical results, that is, a high oxygen overpotential and good electrochemical behaviour as deduced from the electron transfer rate for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple, the electrode obtained with a five spray-pyrolysis sequence is a good candidate for the oxidation-elimination of organic compounds. To verify the chemical and electrochemical stability of this electrode with time, it was employed as anode for oxygen evolution using a $0.5 \text{ M H}_2\text{SO}_4$ solution at a constant current density of 10 mA cm^{-2} (Fig. 4, squares). It can be seen that after 4 h electrolysis the difference $E(t) - E(t=0)$ increased 1 V and reached 4.5 V after 5 h. Figure 1, dashed line, shows the voltammogram of this electrode in H_2SO_4 after 5 h of electrolysis. The voltammetric profile of this electrode has changed showing a decrease in current for all potentials. Also, the oxygen evolution has shifted to more positive potentials. Figure 5, solid line, shows the voltammetric behaviour of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox system on this electrode. The voltammogram has dramatically changed, showing a large decrease in the value of the anodic and cathodic current peaks and a shift of these peaks to more positive and negative potentials, respectively. The separation between peak potentials is now 600 mV instead of 96 mV (Fig. 2). This result clearly shows that the electrode has lost its electrocatalytic activity after working in sulphuric acid for 5 h.

A plausible explanation for this behaviour is the formation of a passivating layer at the substrate-film interface [5], which imparts low conductivity to the electrode [9]. This passivating layer may be formed because the electrolyte solution is in contact with the titanium substrate due to the small thickness of the film (lower than approximately $1 \mu\text{m}$) or its high porosity.

The stability of the electrode can be improved by increasing the thickness of the SnO_2 film by increasing the number of spray-pyrolysis sequences. The

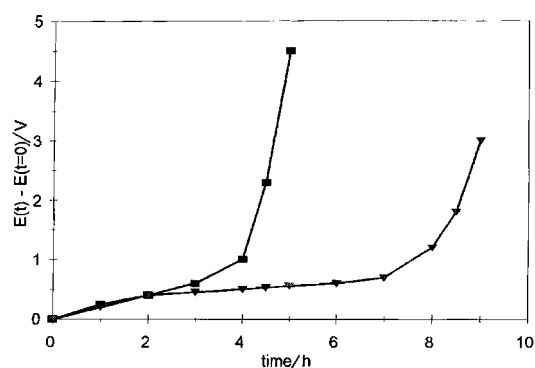


Fig. 4. $E(t) - E(t=0)$ against electrolysis time in $0.5 \text{ M H}_2\text{SO}_4$ for SnO_2 electrodes doped with antimony with: (■) five spray-pyrolysis sequences, (●) nine spray-pyrolysis sequences. $j = 10 \text{ mA cm}^{-2}$.

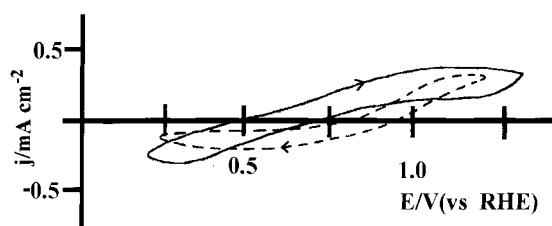


Fig. 5. Voltammetric behaviour of SnO_2 electrodes doped with a five spray-pyrolysis sequence in $5 \times 10^{-2} \text{ M FeSO}_4 + 0.5 \text{ M H}_2\text{SO}_4$. Key: (—) SnO_2 doped with antimony after 5 h of electrolysis at 10 mA cm^{-2} ; (---) SnO_2 doped with antimony and platinum after 60 h of electrolysis at 40 mA cm^{-2} . $\nu = 50 \text{ mV s}^{-1}$.

initial electrochemical behaviour of a SnO_2 electrode doped with antimony obtained after nine spray-pyrolysis sequences is similar to that obtained after five sequences (Figs 1 and 2, solid line). However, the stability of the electrode measured as the time for obtaining $E(t) - E(t=0) > 1 \text{ V}$, increases from 5 to 9 h of electrolysis at 10 mA cm^{-2} in $0.5 \text{ M H}_2\text{SO}_4$ (Fig. 4, triangles).

3.2. SnO_2 electrodes doped with antimony and platinum

It has been shown that the electrocatalytic activity and the resistance to corrosion of these types of electrode can be increased if mixed oxides are used [16]. One of these oxides is the active component while the other improves resistance to anodic dissolution. The preparation procedure is crucial in determining the final properties.

For this reason, another possible method for enhancing the stability of the electrode, in addition to the thickening of the SnO_2 film, is to obtain coatings of mixed oxides of tin and platinum on titanium substrate. Figure 6, solid line, shows the voltammogram in a $0.5 \text{ M H}_2\text{SO}_4$ solution for a SnO_2 electrode doped with antimony and platinum prepared with a five spray-pyrolysis sequence with a $10\% \text{ SnCl}_4 \cdot 5\text{H}_2\text{O} + 1\% \text{ SbCl}_3 + 0.42\% \text{ H}_2\text{PtCl}_6$ in ethanol-HCl mixture. The oxygen evolution is shifted to less positive potentials than those obtained with a SnO_2 electrode doped only with antimony (Fig. 1, solid line). During the negative sweep a small peak near 0.6 V is also obtained, which could be associated

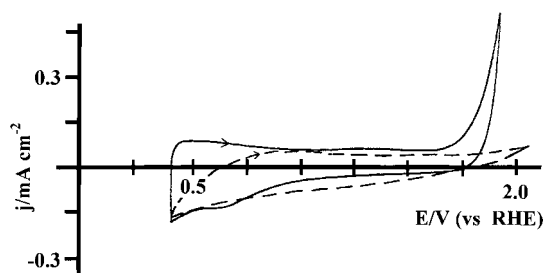


Fig. 6. Voltammetric behaviour of a SnO_2 electrode doped with antimony and platinum with a five spray-pyrolysis sequence in $0.5 \text{ M H}_2\text{SO}_4$. Key: (—) before and (---) after 60 h of electrolysis at 40 mA cm^{-2} . $\nu = 50 \text{ mV s}^{-1}$.

with the presence of platinum because this peak does not appear in a SnO_2 electrode without platinum (Fig. 1, solid line).

Figure 2 (dashed line) shows the voltammogram for this electrode in a $0.5 \text{ M H}_2\text{SO}_4 + 0.05 \text{ M FeSO}_4$ solution. Good behaviour with respect to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple is observed. The ΔE_p values are very similar to those obtained with a platinum electrode. Figure 7 (circles) shows the stability of the $\text{SnO}_2\text{-Sb-Pt}$ (0.2%) electrode (five spray pyrolysis) in electrolysis at a constant current density of 40 mA cm^{-2} in a $0.5 \text{ M H}_2\text{SO}_4$ solution. The electrode potential increases by 1 V from the initial value after 60 h of electrolysis. Figures 5 and 6 (dashed lines) show the voltammograms for this electrode after 60 h of electrolysis in $0.5 \text{ M H}_2\text{SO}_4 + 0.05 \text{ M FeSO}_4$ and $0.5 \text{ M H}_2\text{SO}_4$ solutions, respectively. The voltammograms clearly show a decrease in electrocatalytic activity for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ reaction with electrolysis time.

If the number of pyrolysis processes is increased to 15 and the proportion of platinum in the spray solution also increases from 0.2 to 1% the voltammetric behaviour is similar to that obtained with the latter electrodes but the stability increases. Figure 7 (triangles) shows that the life time of this electrode is now of 425 h for an electrolysis at 40 mA cm^{-2} in $0.5 \text{ M H}_2\text{SO}_4$. The lifetime of the electrode for electrolysis experiments conducted in neutral solution ($0.5 \text{ M K}_2\text{SO}_4$) at a constant current density of 40 mA cm^{-2} , is approximately 760 h (Fig. 7, squares).

Figure 8 shows the morphological details of the surface of the electrode obtained from a $10\% \text{ SnCl}_4 \cdot \text{H}_2\text{O} + 1\% \text{ SbCl}_3 + 2.1\% \text{ H}_2\text{PtCl}_6$ ethanolic-HCl mixture and fifteen spray-pyrolysis processes on a wire titanium substrate. The surface presents a uniform distribution of particles and is more granulated and spongy than that obtained for a SnO_2 electrode doped with antimony and a five spray-pyrolysis sequence (Fig. 3).

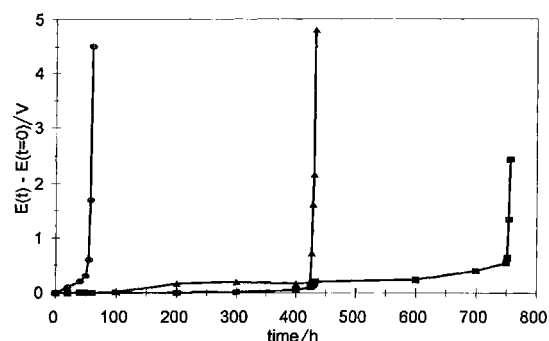


Fig. 7. $E(t) - E(t=0)$ against time of electrolysis for SnO_2 electrodes doped with antimony and platinum with: (●) five spray-pyrolysis sequences from a $10\% \text{ SnCl}_4 + 1\% \text{ SbCl}_3 + 0.42\% \text{ H}_2\text{PtCl}_6$ in ethanol + HCl solution in $0.5 \text{ M H}_2\text{SO}_4$, (▲) fifteen spray-pyrolysis sequences from a $10\% \text{ SnCl}_4 + 1\% \text{ SbCl}_3 + 2.1\% \text{ H}_2\text{PtCl}_6$ in ethanol + HCl solution in $0.5 \text{ M H}_2\text{SO}_4$ and (■) fifteen spray-pyrolysis sequences from a $10\% \text{ SnCl}_4 + 1\% \text{ SbCl}_3 + 2.1\% \text{ H}_2\text{PtCl}_6$ in ethanol + HCl solution in $0.5 \text{ M K}_2\text{SO}_4$. $j = 40 \text{ mA cm}^{-2}$.

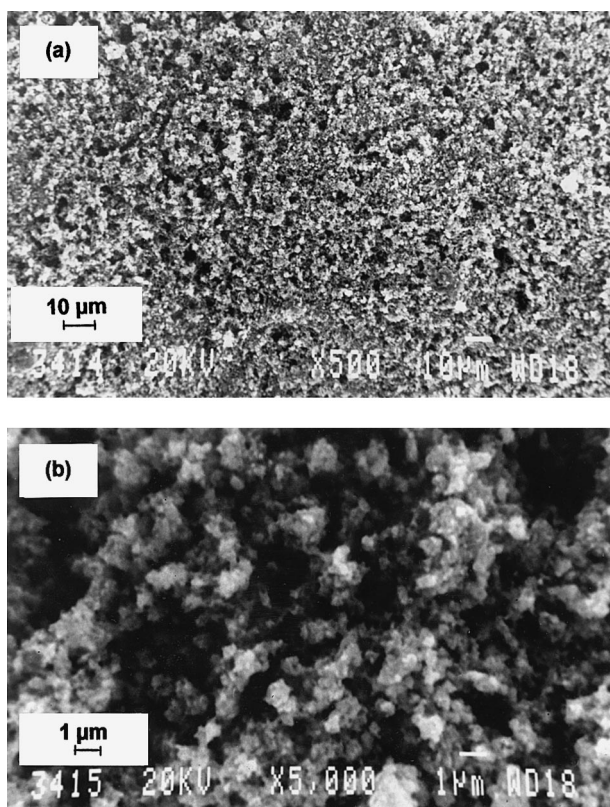


Fig. 8. SEM of a new SnO_2 electrode doped with antimony and platinum with a fifteen spray-pyrolysis sequence.

Titanium is not detected in the EDX analysis for this electrode and only tin, antimony and platinum are present in a proportion of 30.1, 51.5 and 18.4%, respectively. These data also indicate that the thickness of the doped SnO_2 film is higher than $2\text{ }\mu\text{m}$. In fact, profilometric measurement yielded a film thickness of approximately $4\text{ }\mu\text{m}$.

Figure 9 shows two photomicrographs of this electrode after 760 h of electrolysis in $0.5\text{ M K}_2\text{SO}_4$ at 40 mA cm^{-2} . The surface morphology of the electrode has changed and is smoother. The results of the EDX data show a change in electrode composition, titanium now being detected. Tin, antimony, platinum and titanium are present in a proportion of 25.5, 34.3, 23.1 and 14.1%, respectively.

For industrial electrodes to be used in filter-press cells, additional experiments were carried out with electrodes prepared on titanium sheet and expanded titanium. The electrolysis of a $0.5\text{ M H}_2\text{SO}_4$ solution at 100 mA cm^{-2} was carried out using a Ti(expanded)/ SnO_2 electrode doped with 1% antimony and 1% platinum. The lifetime of this electrode increased to 1800 h, a value substantially higher than that obtained previously (425 h) even using a current density 2.5 times higher.

3.3. XPS characterization

XPS analysis was carried out to gain more information about the nature of the surface of the electrode before and after prolonged oxygen evolution. Figure 10 shows the XPS spectra for an electrode of

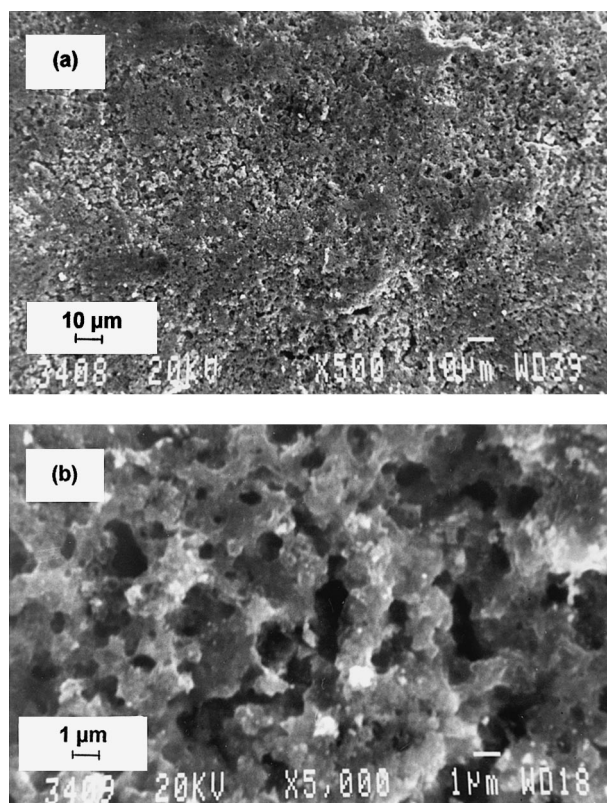


Fig. 9. Scanning electron micrograph of a SnO_2 electrode doped with antimony and platinum with a fifteen spray-pyrolysis sequence after 760 h of electrolysis in a $0.5\text{ M K}_2\text{SO}_4$ solution at 40 mA cm^{-2} .

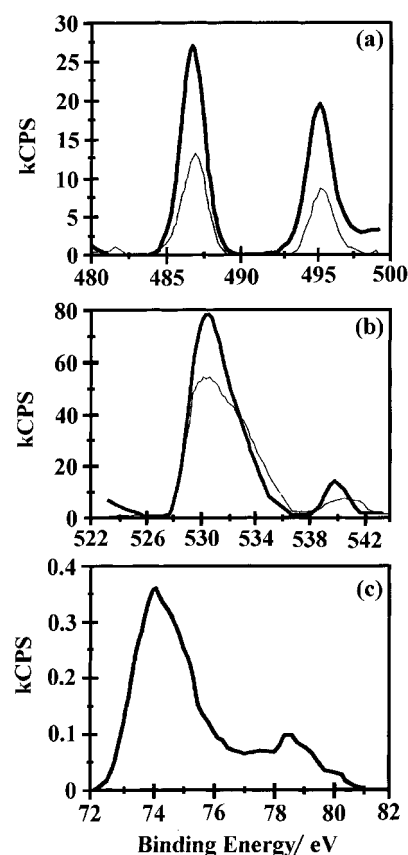


Fig. 10. XPS spectra of a doped SnO_2 electrode, obtained with a fifteen spray-pyrolysis sequence from $10\% \text{ SnCl}_4 \cdot 5\text{H}_2\text{O} + 1\% \text{ SbCl}_3 + 2.1\% \text{ H}_2\text{PtCl}_6$ in ethanol + HCl mixture, before the electrolysis process (thick line) and after 760 h of electrolysis in $0.5\text{ M K}_2\text{SO}_4$ at 40 mA cm^{-2} (thin line). (a) $\text{Sn}(3d_{5/2})$; (b) $\text{Sb}(3d_{5/2})$

Table 1. Binding energies of XPS spectra of Sb 3d_{5/2}, Sn 3d_{5/2} and Pt 4f_{7/2}, corresponding to the SnO₂ electrode of Fig. 10, doped with antimony and platinum with fifteen spray-pyrolysis processes before electrolysis process

	Sb 3d _{5/2}	Sn 3d _{5/2}	Pt 4f _{7/2}
BE/eV	530.4	486.7	74.1

Table 2. Binding energies of the XPS spectra of Sb 3d_{5/2}, Sn 3d_{5/2} and Pt 4f_{7/2}, corresponding to [17]

	O 1s	Sn 3d _{5/2}	Sb 3d _{5/2}	Pt 4f _{7/2}
SnO ₂	530.6	486.6		
SnO		486.9		
H ₂ O	533.1			
Sb			528.2	
Sb ₂ O ₃			530.0	
Sb ₂ S ₅			529.3	
Sb ₂ Cl ₅			530.9	
Pt				71.2
PtO				74.2
PtO ₂				75.0

SnO₂ doped with antimony and 1% platinum, obtained with a fifteen spray-pyrolysis sequence, before and after oxygen evolution for 760 h at 40 mA cm⁻² in 0.5 M K₂SO₄. Before electrolysis the characteristic bands of Sn, O, Sb and Pt are visible in the spectra (untreated electrode, thick line). The features corresponding to Sb(3d_{5/2}) and O(1s) overlap in Fig. 10(b). It is noteworthy that titanium was not detected on the surface either before or after electrolysis. Table 1 shows the binding energies corresponding to the features of Sb(3d_{5/2}), Sn(3d_{5/2}) and Pt(4f_{7/2}) for the untreated electrode. The comparison of the binding energy of Sn(3d_{5/2}) and Sb(3d_{5/2}) with data from [17] (Table 2) indicates that the oxidation state of tin and antimony are +4 and +3, respectively, probably as SnO₂ and Sb₂O₃. In [11] and [12] the authors indicate that the oxidation state of tin and antimony are +4 and +5, respectively, as SnO₂ and Sb₂O₅. In the case of platinum, the binding energy corresponds to a +2 oxidation state, probably PtO. Figure 10, shows the same features for the electrode after oxygen evolution (treated electrode, thin line). The oxidation state of Sn and Sb has not changed due to by oxygen evolution. In the case of Sb(3d_{5/2}) and O(1s), (Fig. 10(b)) a broadening of the overlapped peak to higher binding energies is observed. This indicates that hydroxides and water are present in the outermost layer, this probably being responsible for the loss of electrocatalytic activity. This is in agreement with results of Kötzt *et al.* [5] who suggest hydration of SnO₂ as the cause of deactivation. After electrolysis, platinum has been detected only at trace level.

4. Conclusions

Doped SnO₂ electrodes were prepared by the standard spray pyrolysis method. SnO₂ electrodes doped

with antimony with and without platinum were characterized by cyclic voltammetry. The Fe³⁺/Fe²⁺ redox couple was used to test the electrocatalytic activity of the various electrodes.

Oxygen evolution process in 0.5 M H₂SO₄ and 0.5 M K₂SO₄ solutions was used for testing the stability of the different doped SnO₂ electrodes. It was shown that an increase in the number of spray-pyrolysis sequences does not improve the electrocatalytic properties of the electrodes. However, the thickness of the film increases, and hence the stability of the electrode.

The presence of platinum in the SnO₂-Sb electrode also increases its stability. Thus an electrode prepared using a 10% SnCl₄.5H₂O + 1% SbCl₃ + 2.1% H₂PtCl₆ ethanolic-HCl mixture and a fifteen spray-pyrolysis sequence on an expanded titanium substrate has a lifetime of 1800 h in 0.5 M H₂SO₄ at 100 mA cm⁻².

The XPS results show that the oxidation state of the Sn, Sb and Pt in a SnO₂ electrode doped with these two latter metals, are +4, +3 and +2 probably as SnO₂, Sb₂O₃ and PtO, respectively.

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